CONDUCTING POLYMER COATINGS - RECENT ADVANCES

D. C. Trivedi

Electrochemical Materials Science Division, Central Electrochemical Research Institute, Karaikudi - 630 006, India.

Recent progress made in the area of conducting polymers is reviewed with emphasis on new experimental results that focus on how to tailor fundamental properties of conducting polymers for desired technological application.

INTRODUCTION

The discovery that the electronic conductivity of polyacetylene can be enhanced by many orders by doping in 1977 provided impetus for research in conducting polymers which was recognised by the award of the Nobel prize to Heeger, Mac Dermid and Shirakawa for the year 2000. Conducting polymers differs from other materials at least in two aspects: conductivity can be tailored and its property can be modulated by simple methods of organic chemistry.

These new types of organic polymers have the remarkable ability to conduct electrical current and are known as conducting polymers or nick-named as synthetic metals, and are finding practical applications in rechargeble batteries, electrolytic capacitors, bio-sensors, flexible light emitting diodes, smart windows and in dissipation of static electricity and in control of electromagnetic radiations. The envisaged applications are many with a tremendous potential for future scientific and technological development. The excitement about these relatively new materials is high because of the novelty of the concept that plastics, which are free from corrosion, can be shaped and can perform the function of either metals or semiconductors or as an insulator by the process of doping.

The basic requirement of these systems to achieve electronic conductivity is conjugation to yield a band structure. Here in these polymers valence electrons are completely delocalised and move almost freely through the crystal lattice. Common polymers generally consist of saturated carbon atoms covalently bonded to each other, thus valence electrons in such molecules are all shared between bond forming atoms and are held tightly. In these saturated backbone polymers electrons are not capable of providing any charge carrier or a path for charge carrier movement through the chain and hence behave as electrical insulators. It is therefore apparent that extensive delocalisation of electrons in the polymer backbone is necessary for a polymer to behave as an electrical conductor. This delocalisation of electrons may occur through the interaction of π-bonded electrons in a highly conjugated chain or by a similar interaction of π - electrons with non-bonded electrons of electron rich hetero atoms (e.g. S, N, O, etc.)

HISTORICAL SURVEY OF ELECTRONIC CONDUCTIVITY IN ORGANIC SOLIDS

The electrical conductivity in organic compounds is not a new phenomenon and was first reported by Mecoy and Moore (1911) that organic amalgams like ammonium amalgam and mono methyl ammonium amalgam have true metallic properties. This is the first published report, which indicates that organic compounds are capable of yielding a binary

alloy like any metal. The metallic properties in a binary alloy are formed with true metallic properties only from components, which are true metals. These authors proved that the organic radicals in an amalgam are in metallic state and that it is possible to prepare composite metallic substances from non-metallic constituent elements.

Nearly forty years later Akamatu etal. (1954) reported that some complexes between polycyclic aromatic compounds like perylene and halogens such as bromine yields a salt in the solid state having fairly good electrical conductivity of ~ 1-10 ^{3}S/cm. This high electrical conductivity is due to the formation of a charge transfer complex. Similarly, Kallmann and Pope (1959) observed a change in bulk conductivity in anthracene and iodine / NaI system, where the change in conductivity was attributed due to the extraction of electrons from anthracene by iodine, thus creating a positive hole in the anthracene which travels under the action of the field through the crystal to the negative electrode.

Some organic charge transfer complexes having ordered stacks or columns of donor and acceptor molecules exhibit enhanced electrical conductivity and at low temperatures superconducting transitions. Short intra stack distance in such complexes permits overlap of molecular orbital on adjacent sites, which result in the delocalisation of unpaired electrons and in a very narrow metallic energy band. The majority of organic conducting polymers have been synthesised from aromatics except polyacetylene, which is one of the simplest conjugated systems as shown in Fig. 1. The basic drawback of polyacetylene is its environmental instability due to degenerate ground state, making its practical application difficult, whereas poly aromatics offer advantages over polyacetylene by way of flexibility in structure and are environmentally stable and can be used under ambient conditions as shown in Fig. 2.

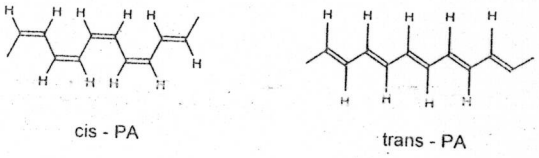


Fig. 1 - Structures of *cis* and *trans* - PA

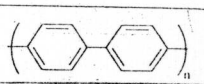
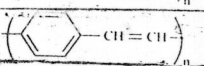
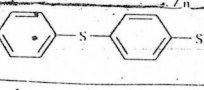
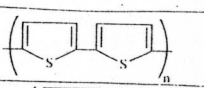
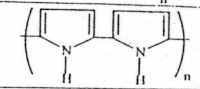
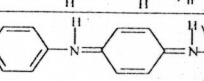
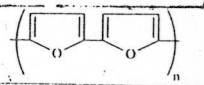
S. No	Conducting polymer	Structure
1.	Poly(*p*-phenylene)	
2.	Poly(phenylene vinylene)	
3.	Poly(phenylene sulphide)	
4.	Poly (thiophene)	
5.	Poly (pyrrole)	
6.	Poly (aniline)	
7.	Poly (furan)	

Fig. 2 - Structures of polyaromatics

The maximum electronic conductivity of some of the well-known conducting polymers is given in Table I.

Table I

Polymer	Conductivity (S/cm)
Polyacetylene (PA)	1.42 x 10^{5}
Poly (*p*- phenylene) (PPP)	1000
Poly (phenylene sulphide) (PPS)	100
Poly (phenylene vinylene) (PPV)	1000
Polypyrrole (PPy)	100
Polythiophene (PTh)	100
Polyaniline (PAn)	100

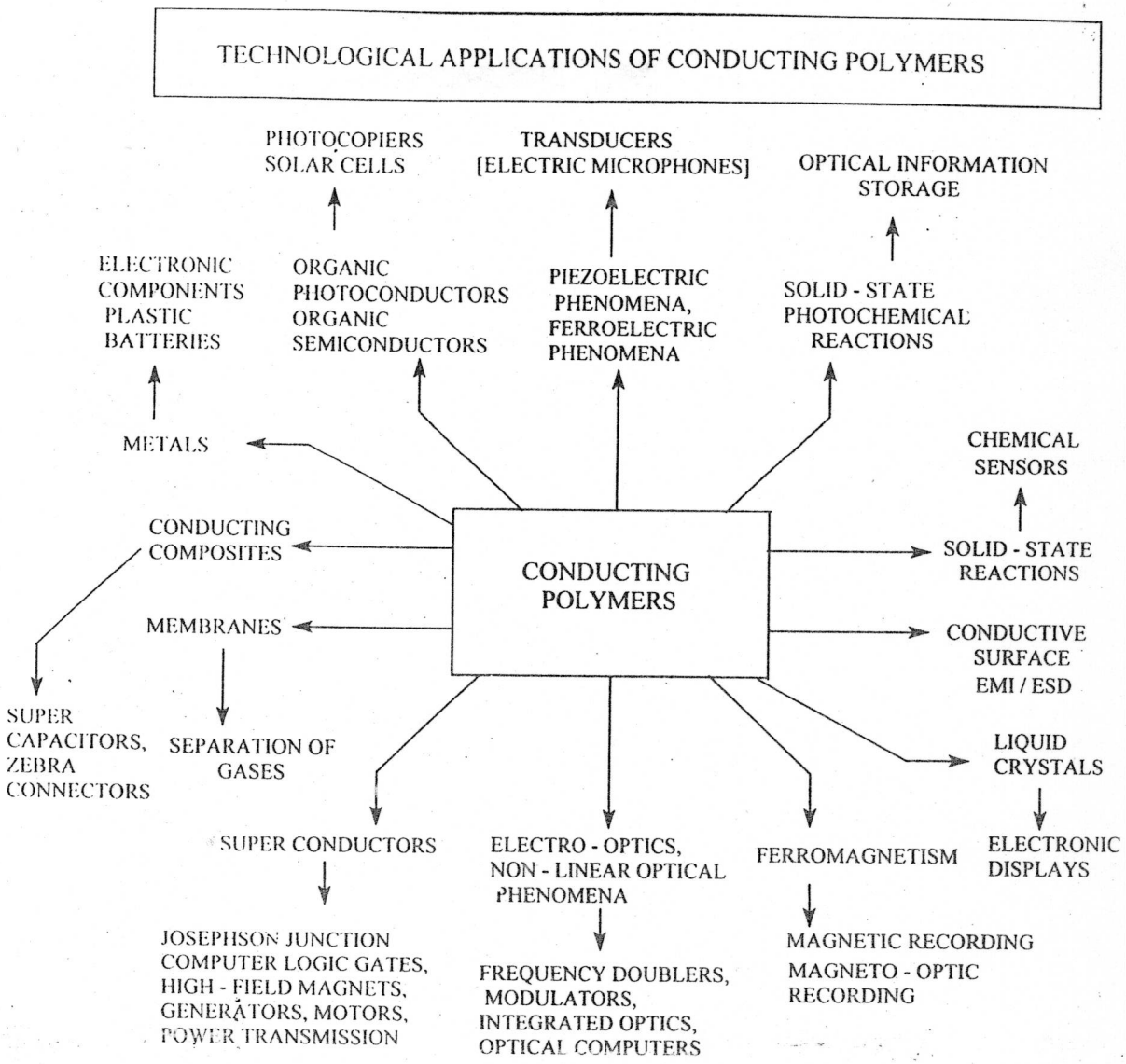


Fig. 3 - Technological applications of conducting polymers

On undoping, these polymers behave like an insulator and depending upon the level and type of doping the conductivity can be modulated to suit the applications. These exotic materials, due to their tunable properties, have been investigated for various devices. These materials need protection from air and humidity to achieve higher lifetimes. Protection methods are being developed for light emitting diodes [LED] as well as for photovoltaics. The effectiveness of protection system is crucial for the success of any application using

these materials. A recent survey indicates that stability problem in LED has been sufficiently overcome in order to enter into large-scale applications. It is intriguing to think of these materials for thin film photovoltaics. The flexibility offered through the chemical tailoring of desired properties, as well as cheap technology would make them a most preferred material. The close packing of electronic components in a limited space has created the new form of pollution known as electronic noise pollution and at present to control them metal/carbon composites are in vogue. The metal incorporated composites suffer from galvanic corrosion and thereby may damage the electronic device and carbon composites are brittle and thus would cause problem of continuity of the shield. Thus, their replacement by conducting polymer would help to resolve these twin problems associated with metal and carbon composites. Fig. 3 shows some of the technological applications of conducting polymers.

Conducting surfaces made out of conducting polymers are it non corrosive in nature and of low density. The separation of oxygen and nitrogen is based on magnetic property of the gases and not on size and hence 100% separation is achieved.

Polyaniline (PAn) is a typical phenylene - based polymer having a chemically flexible -NH- group in a polymer chain flanked on either side by a phenylene ring. The protonation and deprotonation and various other physicochemical properties of PAn can be attributed to the presence of - NH - group. PAn is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black (Letheby, 1862). At the begining of the 20th century organic chemists began investigating the constitution of aniline black and its intermediate products. Willstatter and Moore (1907, 1909) regarded aniline black as an eight - nuclei chain compound having an indamine structure (Fig. 4).

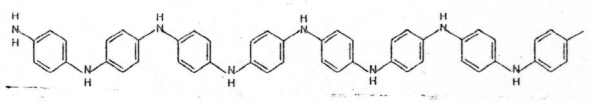


Fig. 4 - Indamine structure

Polyaniline as a conducting polymer has generated tremendous interest among chemists, physicist and material scientists due to:

1. Ease of synthesis
2. Environmental stability
3. Simple non-redox doping by protonic acids
4. Starting material aniline is a cheap, bulk chemical.

Green and Woodhead (1910) were able to report various constitutional aspects of aniline polymerisation. The conclusions of their study were as follows :

1. There are four quinoid stages derived from the parent compound leucoemeraldine.
2. The minimum molecular weights of this primary oxidation of aniline are in accordance with an eight - nuclei structure.
3. The conversion of emeraldine into nigraniline consumes one atom of oxygen.
4. The conversion of emeraldine into pernigraniline consumes two atoms of oxygen.
5. The conversion of nigraniline into pernigraniline consumes one atom of oxygen.
6. The reduction of emeraldine to

leucoemeraldine consumes four atoms of hydrogen.

7. The reduction of nigraniline to leucoemeraldine consumes six atoms of hydrogen.

8. The reduction of pernigraniline to leucoemeraldine consumes eight atoms of hydrogen.

These authors carried out oxidative polymerisation studies using mineral acids and oxidants such as persulphate, dichromate and chlorate and determined the oxidation state of each constituent by redox titration using $TiCl_3$. They also extended their studies on the oxidative polymerisation of *o*- and *p*-chloroaniline and *o*-anisidine and reported that dimethylaniline remained unattacked under these experimental conditions. Almost 50 years later, Surville et al. (1968) reported proton exchange and redox properties with the influence of water on the conductivity of PAn. However, interest in PAn was generated only after the fundamental discovery in 1977 that iodine doped polyacetylene has a metallic conductivity (Shirkawa et al., 1977) which triggered research interest in new organic materials in the hope that these would provide new and / or improved electrical, magnetic, optical material or devices.

Polyaniline is prepared either by *chemical* or *electrochemical* oxidation of aniline under acidic conditions. An aqueous medium is preferred. The synthesis of polymer by either chemical or electrochemical methods depends upon the intended application of the polymer. Whenever thin films (on electrode surface) and better ordered polymers are required, an electrochemical method is preferred. PAn synthesized by chemical or an electrochemical route has the four forms shown in Fig. 5.

Conducting polypyrole (PPY) Fig. 2 has been of great interest because of its good stability and its easy preparation by electro-polymerisation.

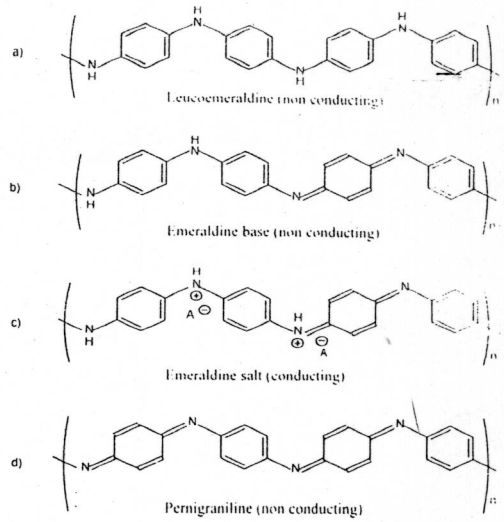


Fig. 5 - Various forms of PAn

It has attracted equal attention from physicists and chemists, because of its simplicity of structure and low oxidation potential which favours the formation of 2, 5- bonded polymer as a free standing film on an anode surface.

Polypyrrole(PPy) is known since 1916 (Angeli, 1916); however its semiconducting properties were first investigated by McNeill et al. (1963). The polymerisation can be carried out chemically as well as electrochemically. Chemically, pyrrole can be oxidatively polymerised in both solution and vapour phase (Street et al., 1982). PPy was first electrochemically synthesized as a black powdery deposit in aqueous sulphuric acid medium anodically by Dall' Olio et al. (1968). Diaz et al. (1979) reported electrochemical synthesis of an electrically conducting material with facilitated incorporation of a variety of counter ions into the polymer film. Since the oxidation potential of PPy is lower than that of monomer, thus the polymer is simultaneously oxidised during polymerisation and hence counter ions from electrolyte are incorporated into growing

polymer in order to maintain electrical neutrality.

Polypyrrole can be viewed as a carbon chain with structure of polyacetylene stabilised by the heteroatom and has a non-degenerate ground state related to non-energetic equivalence of two limiting mesomeric forms, aromatic and quinoid. The polypyrrole films were synthesized electrochemically from 0.1 molar solution of pyrrole in aq. 1M solution of sodium salt of aromatic sulphonic acid (e.g. AQSA). The electrolyte was purged with nitrogen before electrodeposition. The electrodeposition was carried out on a stainless steel plate of 25 cm width, 45 cm length and 2mm thickness, the cathode was titanium plate of same dimensions. The voltage was 3V and current density 1.0 mA/cm^2. After deposition the electrodes were dried at 50°C under vacuum and the films were peeled off.

Polymerisation Mechanism : In polymerisation of pyrole, the first step consists of the oxidation of the monomer to its radical cation. The second step involves the coupling of two radical cations to yield a dihydrodimer dication that leads to a dimer after losing two protons and rearomatisation. The dimer has less oxidation potential than the monomer, undergoing further coupling with a monomeric radical. Subsequently, electrochemical and chemical steps occur until oligomer becomes insoluble in the electrolyte and precipitates on the electrode surface. The polymerisation process requires 2.2 - 2.4 Faraday/mole. 2 Faraday are required to generate the macrocation. Thus, this corresponds to reversible oxidation (doping) of the polymer. The polymerisation mechanism is shown in Fig.6.

Doping - dedoping is a complex phenomenon governed by many factors, such as ion pairs formation which can occur within the doped polymer between the dopant and positive charge on the polymer chain, resulting in the diffusion of cation from electrolyte to keep polymer chain electrically neutral. These cationic species owing to their smaller ionic size have greater mobility; therefore continuous doping-dedoping by cycling the polymer electrode between extreme potential limits yields a polymer free from ion pair as well as from oligomeric impurities. Therefore, it is inevitable that kinetics of doping-dedoping and polymerisation is influenced by steric effects associated with the counter ion, such as :

- Adsorption on working electrode
- Redox potential
- Ionic charge
- Ionic size
- Solvation shell
- Ionisation constant of the electrolyte
- Concentration of the electrolyte
- Electrochemical potential of doping.
- Diffusion co-efficient of a dopant, which varies with solvent, concentration of electrolyte, temperature and applied potential.

These aspects are important because polymer undergoes substantial volume changes during doping and dedoping processes, Baughman (1996) reported that these dimensional changes influence mechanical strength of a polymer and have been utilised to convert electrical energy to mechanical energy. Not all dopants can induce charge transport in the polymer. The charge transport depends upon the redox energy of the host and guest molecules because transfer of an electron is from high to low redox energy. Initially the charge transfer on doping is between the dopant molecule and the proximal polymer site, but subsequently some diffusion of polymer charge to the dupant site can be expected, generating thereby pair states in the

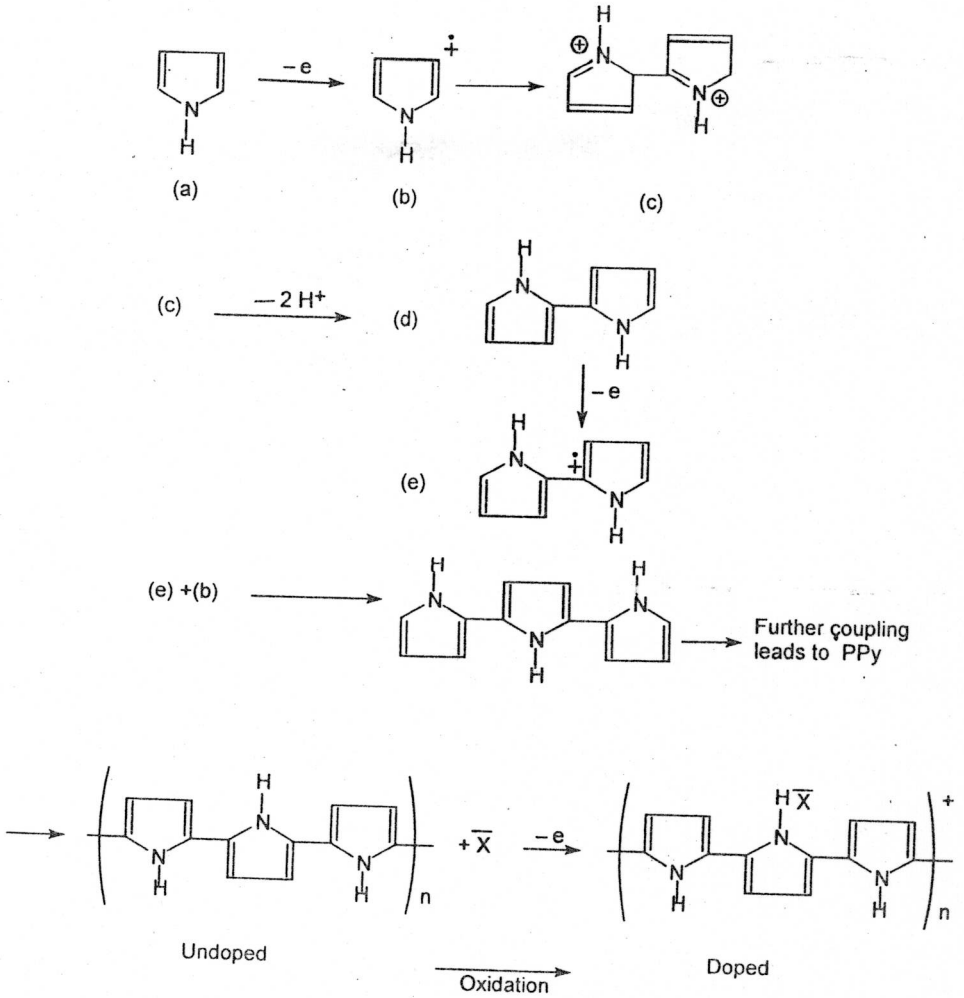


Fig. 6 - Polymerisation mechnism of pyrrole to polypyrrole

polymer. In equilibrium, the numbers of polymer pair states are equal to the number of ionised dopants. ESR (Javedi et al., 1988), electron energy loss spectroscopy (Litzemann et al., 1989), NMR (Raghunathan et al 1996) and thermopower studies (Raghunathan et al., 1993) support these findings. These observations show that ferromagnetism can be induced in these conjugated systems.

Synthesis Of Polyaniline : Ammonium peroxydisulphate (0.1M aqueous solution in HCl) was added dropwise to a stirred solution of 0.1M aniline dissolved in 1M aqueous solution of HCl, that was pre-cooled to a temperature in the range 0-5 °C. Ammonium peroxydisulphate was added very slowly to prevent warming up of the solution. After completion of the addition (addition time almost 4-6hrs.), stirring was continued for 2 hrs to ensure completion of the reaction. At the end of the reaction acetone was added to terminate the polymerisation reaction and the mixture was filtered under suction. Collected green precipitates of emeraldine hydrochloride were

washed repeatedly with distilled water till these washing were colourless. The filtered and washed precipitates were then treated with aqueous solution of ammonia (pH ≈ 9) under stirring for 6 - 8 hrs for effective undoping to obtain emeraldine base. This reaction mixture was filtered and washed with distilled water until washings were neutral to a pH indicator paper.

The blue emeraldine base powder, obtained after filtration, was purified by refluxing with methyl alcohol, benzene and acetone. This process of treatment with organic solvents was repeatedly done till the filtrate was colourless. Finally, the blue emeraldine base obtained was dried under dynamic vacuum at 60-80 °C for 8 hrs.

The fine powder of blue emeraldine base thus obtained was dispersed in 1M aqueous solution of functionalised aromatic sulfonic acids like CSA or DBSA under vigorous stirring for 24 hours. After doping reaction, solution was filtered under suction and collected material was given washing with 1M aqueous solution of functionalised aromatic sulfonic acid.. By this method, a doping level of 50 mole percent was achieved. The so obtained polymer was dried at 60-80 °C under dynamic vacuum for 12 hrs. (Trivedi, 1997).

In a 100ml beaker, required amount of emeraldine base (1mole), functionalised organic sulphonic acid (0.5 mole) and halo-substituted functionalised phenol (ranging from 0.4 mole to 2 moles depending upon the dopant used) are mixed in the presence of any one of the following organic solvents: benzene, $CHCl_3$, toluene or xylene. By mechanical grinding for 1 to 2 hrs., a slurry is obtained which yields a flexible freestanding film on drying under ambient laboratory conditions for 24 to 46 hrs or on drying under dynamic vacuum at 50 to 70 °C for 7 to 8 hrs., (Geetha et al., 2000). The thickness of the as-obtained film was measured by using magnetic coating thickness guage (MIKRO TESTER IV, Model No. F171/100).

The substrate materials used for grafting were E-glass fabric, glass wool and nylon cloth. In this study E-glass fabrics were mainly used for grafting. First they are subjected to thorough cleaning using sodium carbonate solution to remove foreign materials. Then these substrates were rinsed in distilled water. Aliphatic anhydride in organic solvents like ethyl methyl ketone, methanol, acetone solution was prepared and the E-glass fabrics were dipped in that solution for half an hour to one hour. This was done to strengthen the E-glass fabric used for grafting.

The E-glass fabrics were immersed in 0.1 molar solution of aniline in organic sulphonic acid media and the pH was maintained between 1-2. The above-mentioned organic sulphonic acids were used for grafting the E-glass fabric. To the double walled tray (30 x 40cm) containing the reaction mixture and substrate, the stoichiometric amount of 0.1M aqueous solution of ammonium peroxydisulphate was added slowly. During the reaction, temperature was maintained at 5-10 °C by circulating ice-cold water. The substrates were rotated constantly in a mechanical shaker to ensure the uniformity of reaction at the solid/liquid interface. After 1 hour the substrates were removed and rinsed thoroughly with distilled water. Two or three times grafting was required to achieve good conductivity. The final washings were done with 0.1 mole aqueoeus solutions of the dopant acids and dipped in that solution for 1 hour and dried under ambient laboratory conditions (Trivedi and Dhawan, 1992, 1993).

We have shown that polyaniline can yield a freestanding film using the concept of secondary doping and this film can be used for the control of electromagnetic radiations and many other devices including sensors (Satheesh Kumar et al., 2000).

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